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Dual-Mode Diffusion of Argon Confined in Carbon Nanotube Bundles

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1. Introduction

Diffusion of host molecules in nano-porous materials plays a central role in many practical applications. However effective control of transport in nanostructures requires a deep understanding of the diffusion mechanisms involved. The mechanisms by which molecules flow through nanoporous materials are currently not well understood and are difficult to determine experimentally, especially for materials having a hierarchical pore structure, such as carbon nanotube bundles. However, commonly observed mechanisms include ballistic motion (short times), Fickian diffusion (3 dimensional random walk, long times) and single-file diffusion (molecules cannot pass each other, long times). Hahn and Kärger investigated diffusion in single-file system and deviations from the normal time regime of single-file diffusion [1, 2]. Mon and Percus studied the dynamics of quasi-one-dimensional single-file mobility using a theoretical model [3]. Here we examine the diffusion mechanism in different regions of carbon nanotube bundles as well as the effect of the loading.

2. Simulation Details

The bundle consists of (25,0) SWNTs with interstitial channel diameters of 0.354 nm and geometric pore diameter of 1.95 nm for the (25,0) SWNT [4]. Grand Canonical Monte Carlo (GCMC) simulations were performed to measure the adsorption isotherm of argon at 120 K in the relative pressure range of $P/P_o = 1x10^{-6}$ to 0.1, where P_o is the bulk vapor pressure of argon at 120 K. Periodic boundaries were used in 3 dimensions. Molecular Dynamics (MD) simulations were equilibrated for 1 ns in NVT using a Nosé-Hoover thermostat with a 1 fs timestep, followed by production runs for 10 ns with a 1 fs timestep in the microcanonical ensemble (NVE). MD simulations were performed using the LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) simulation package [5].

3. Results and Discussion

Fig. 1 shows snapshots of Argon in SWNT bundles at different relative pressures at 120 K. At relative pressures lower than 0.00001, the particles adsorb only in the interstitial channels, since these are the strongest adsorption sites. As the pressure increases, the nanotubes begin to fill with adsorbate, until at relative pressures close to 0.00005 the interstitial sites are almost completely filled. The nanotubes channels continue to fill with adsorbate as the pressure increases, and the bundle is almost completely filled at relative pressures close to 0.01.

All 3 mechanisms are seen in our MD simulations. The mean squared displacements are shown in Fig. 1. In all cases we observe ballistic motion at sub-picosecond times, changing to either Fickian or single file motion at longer times, depending on the pore diameter. The pore size distribution is bimodal, with diffusion occurring within the nanotubes and between nanotubes in the interstices. The interstitial channel of 0.354 nm diameter is only slightly larger than the molecular diameter of argon, so the particles in the interstitial sites cannot pass each other. Therefore, we observe all of the interstitial MSDs being proportional to the square root of time, indicating single file diffusion. For fluids

diffusing in the nanotubes, the particles can pass each other and their MSDs are proportional to time, indicating Fickan diffusion. The diffusion coefficients and single-file mobilities decrease with increasing pressure. Although the total MSD of the system depends on both the rates of the diffusing interstitial and nanotube atoms, for P/P_o greater than approximately 0.00001 the total fluid MSD is dominated by the fluid in the nanotube at long times, due to the dramatic difference between the rates of Fickian and single-file diffusion. Thus the total MSD is proportional to time for all except the lowest pressures. The diffusion coefficient of the total fluid decreases until it approaches that for the nanotubes at P/Po = 0.01.

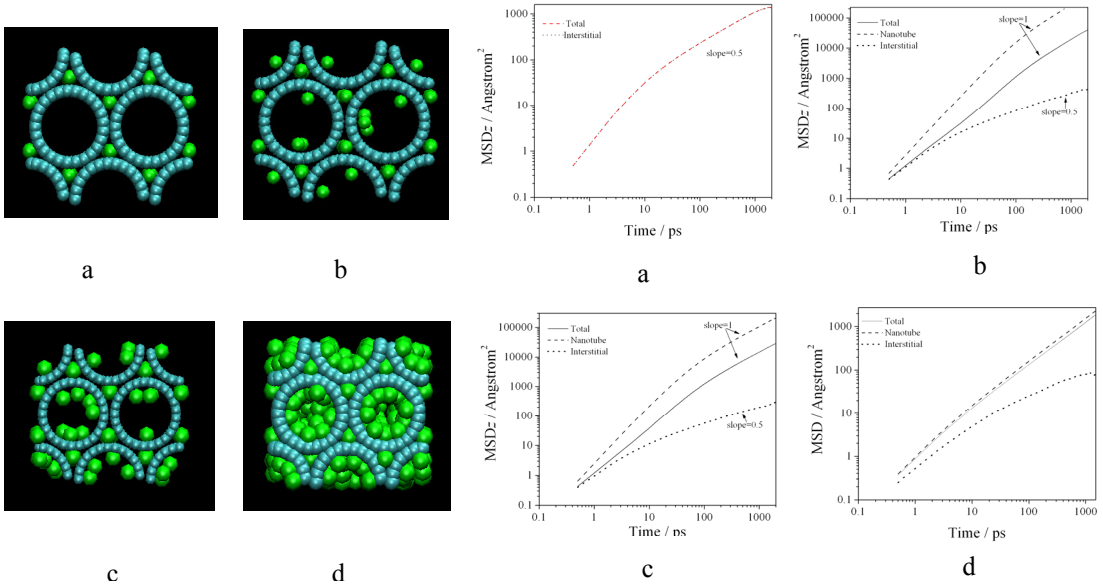

Fig.1 Snapshots (left) and Mean squared displacement (right) of Argon in SWNT bundles at different relative pressures and 120 K. (a) P/P_o = 0.00001 (b) P/P_o = 0.00005 (c) P/P_o = 0.0001 (d) P/P_o = 0.01

4. Conclusion

A dual diffusion mechanism occurs in a (25,0) SWNT bundle. Ar diffuses in single-file in interstitial sites and in a Fickian fashion in the inner nanotube channels. While the adsorption first occurs in the interstices at low pressures followed by pore filling in the nanotubes at higher pressures, the total diffusion of fluid in the bundle is dominated by Fickian diffusion in the nanotubes at longer times for all but lowest pressure. While diffusion in the interstitial sites exhibits a slope of ½ on the log-log plot of MSD vs time, the MSD vs time slope is 1 when fluid has adsorbed in the nanotube channels .

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